BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

As rescanning documents *will not* correct images, please do not report the images to the Image Problem Mailbox.

(19) Europäisches Patentamt
European Patent Office
Office européen de brevets

(11) Publication number: **0 346 055 A2**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 89305671.3

(51) Int. Cl.4: C23C 16/50 , H01J 37/32

(22) Date of filing: 06.06.89

(30) Priority: 06.06.88 JP 138630/88
04.07.88 JP 166599/88
15.08.88 JP 202977/88

(43) Date of publication of application:
13.12.89 Bulletin 89/50

(84) Designated Contracting States:
CH DE FR IT LI NL

(71) Applicant: RESEARCH DEVELOPMENT CORPORATION OF JAPAN
5-2, Nagata-cho 2-chome
Chiyoda-ku Tokyo 100(JP)

(72) Inventor: Okazaki, Sachiko
2-20-11 Takaido-higashi
Suginami-ku Tokyo(JP)
Inventor: Kogoma, Masuhiro
843-15 Shimonlikura
Wako-city Saitam(JP)

(74) Representative: Holmes, Michael John et al
Frank B. Dehn & Co. Imperial House 15-19
Kingsway
London WC2B 6UZ(GB)

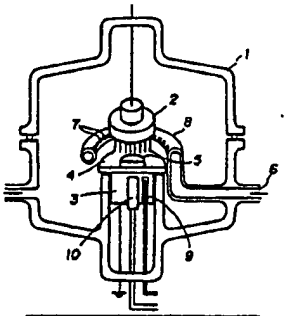
(54) Method and apparatus for causing plasma reaction under atmospheric pressure.

(57) The invention provides a method of treating the surface of a substrate with reactive plasma which comprises exciting a reagent gas in a reaction vessel having a pair of opposing electrodes to produce glow discharge plasma at atmospheric pressure and causing or permitting the plasma to contact the surface of said substrate.

The atmospheric pressure plasma reaction method of the invention can be used for forming a thin film on the surface of a substrate and/or reforming the surface under atmospheric pressure. The invention also provides an apparatus comprising a reaction vessel containing an upper and a lower electrode; the upper electrode may comprise a plurality of vertical fine wires and a solid dielectric may be provided on either or both of the electrodes. A perforated pipe may be provided to assist in uniform distribution of gas near a substrate to be plasma treated.

By using the apparatus having above-mentioned construction, highly stable and uniformly dispersed glow discharge plasma can be obtained at atmospheric pressure without the occurrence of arc discharge, even if the substrate consists of a conductive material, such as a metal or alloy.

FIG. 1



EP 0 346 055 A2

METHOD AND APPARATUS FOR EFFECTING PLASMA REACTIONS AT ATMOSPHERIC PRESSURE

[FIELD OF THE INVENTION]

The present invention relates to a method and apparatus for effecting plasma reactions at atmospheric pressure. More particularly, the present invention relates to a method and apparatus for forming a thin film and/or for reforming (chemically changing) the surface by means of a highly stable glow discharge plasma at atmospheric pressure.

[BACKGROUND OF THE INVENTION]

The film forming methods and surface reforming methods based on low-pressure glow discharge plasma are widely known and industrially applied in various areas. One of the surface treatment methods using low-pressure glow discharge plasma is that known as the organic plasma reaction method for forming a thin film and/or reforming the surface by means of the conversion of an organic compound gas into plasma.

There is available, for example, a method of plasma-exciting a hydrocarbon gas in a vacuum vessel and forming by precipitation an amorphous carbon film on a silicon substrate or a glass substrate, and a method for forming a plasma polymer film of an unsaturated hydrocarbon such as ethylene.

However, all these conventional surface treatment methods based on low-pressure glow discharge plasma require an apparatus and facilities for creating low-pressure conditions because the reaction is to take place under a vacuum of about 1×10^{-5} to 1×10^{-3} torr in all cases, thus resulting in complicated operations and maintenance and high manufacturing costs. A low- pressure method has the further defect of difficult treatment of large-area substrates.

With a view to overcoming these defects in the conventional methods, the present inventor carried out extensive studies and has devised a new film forming and reforming method based on glow discharge plasma at atmospheric pressure thus permitting reduction of costs for apparatus and facilities and facilitating film formation in large-area substrates. The background for this development included the inventor's research on ozone producing silent discharge for many years and analysis of the reaction mechanism regarding plasma film formation.

Furthermore, the present invention is also capable of providing a solution to one problem of glow discharge plasma reactions at atmospheric pressure, namely production of arc discharge when the substrate is a conductive metal or alloy.

More specifically, the present invention provides an improved reaction method based on glow-discharge plasma at atmospheric pressure which makes available, even with a metal or alloy substrate, highly stable plasma of a highly reactive reagent gas at atmospheric pressure.

[BRIEF DESCRIPTION OF THE DRAWINGS]

Fig. 1 is a perspective sectional view illustrating a film forming apparatus having an upper electrode comprising a plurality of fine wires, as an embodiment of the present invention;

Fig. 2 is a sectional view illustrating a typical reaction apparatus of the present invention, in which a solid dielectric is provided for each of the opposing upper and lower electrodes;

Figs. 3 and 4 are bottom views illustrating a typical lower surface of the upper electrode of the present reaction apparatus;

Fig. 5 is a partially cutaway sectional view illustrating another embodiment of the upper electrode the present reaction apparatus;

Fig. 6 is a chart illustrating the relationship between the transvers distance of the substrate and thickness of a thin film deposited on the substrate when a solid dielectric is arranged on each of the upper and lower electrodes;

Fig. 7 is a sectional vi w illustrating further another embodiment of the reaction apparatus in which a solid dielectric is arranged on each of the opposing upper and lower electrodes;

Figs. 8 and 9 are views illustrating an IR absorption spectral chart and an XPS depth profile, r spectively, when forming an SiN_x film with the use of the apparatus of the invention; and

Figs. 10 and 11 are sectional views illustrating further another embodiment of the reaction apparatus of the present invention, in which a solid dielectric is provided on the upper electrode.

[DETAILED DESCRIPTION OF THE INVENTION]

According to the present invention we provide a method of treating the surface of a substrate with reactive plasma which comprises exciting a reagent gas in a reaction vessel having a pair of opposing electrodes to produce glow discharge plasma at atmospheric pressure and causing or permitting the plasma to contact the surface of said substrate.

In the film forming embodiment of the method, the upper electrode is preferably provided with a film formation apparatus which can be suitably used for this method.

The film forming apparatus preferably has an upper electrode consisting of a multiplicity of vertical fine wires, a solid dielectric on the upper surface of a lower electrode on which the substrate is placed and a perforated pipe which uniformly diffuses gas over the surface of the substrate and its vicinity. This is shown in Fig. 1.

The apparatus shown in Fig. 1 comprises a reaction vessel consisting of a bell jar (1) made from Pyrex glass, for example, provided with an upper electrode (2) and a lower electrode (3) to which is applied a high potential difference. The upper electrode (2) consists of a plurality of fine wires arranged vertically. On the upper surface of the lower electrode (3), a solid dielectric (4) or a material such as glass, ceramics or plastics is provided. On this solid dielectric (4), a substrate (5), e..g a flat plate or the like, is placed.

A mixture of inert gas such as He, Ne, Ar, or N_2 and monomer gas such as a hydrocarbon which is a raw material for forming a thin film is introduced through inlet (6) into a perforated pipe (8) having several openings (7) so that the gas mixture diffuses uniformly from openings (7) onto the substrate (5). Unreacted gas, inert gas, etc are discharged from the gas exit of the reaction vessel.

A temperature sensor (9) and a heater (10) are provided in the lower electrode (3). A cooling device can also be installed.

In the film forming apparatus of the present invention which can be indicated in Fig. 1 above, the reaction zone in the bell jar (1) is maintained at substantially atmospheric pressure. Therefore, no vacuum device or similar equipment is required in contrast to a conventional low-pressure glow discharge plasma film formation apparatus.

Inert gases to be used in the reaction, such as He, Ne, Ar, or N_2, can be used as simple substances or as mixtures. However, to prevent arc discharge it is desirable to use He, which has the lowest ionisation potential, to begin the glow discharge. It is possible to form a desired plasma polymer film by using a suitable monomer gas mixed with the inert gas as the raw material for forming the film. The reagent gas may be selected from saturated hydrocarbons such as methane, ethane, etc. unsaturated hydrocarbons such as ethylene, propylene, etc., hydrocarbons having halogen or other functional substituents, semimetals such as Si, Ga, etc., or gaseous metal compounds.

Depending on the gas to be used, halogen, oxygen, hydrogen, nitrogen or ammonia may be mixed for the purpose of accelerating the reaction or as a reaction component for forming a SiN_x film. The ratio of the inert gas to the reagent gas is not specially critical, but the gas concentration is desirably higher than 90%. A mixture of several kinds of gases may be used.

It is desirable to produce a plasma of the gas mixture in a state in which the gas is uniformly diffused and supplied in a plasma zone close to the substrate. To achieve this, the perforated pipe (8) shown in Fig. 1 or other suitable means may be used. Its shape and structure may be selected depending on the size of the apparatus and that of electrodes. Inflow of outside gas (oxygen, nitrogen, etc) must, in general, be prevented.

Plasma is formed by applying a high voltage between the electrodes. The voltage can be determined according to the heat resistance, forming speed, or the like of the film to be formed. The film formation speed can be controlled by adjusting frequency and voltage. For example, as shown in Fig. 1, it is possible to make the film thickness uniform, minimize differences in thickness between the central part and peripheral part of the substrate (5) and enable a stable glow discharge to be formed by using vertical fine wires for the upper electrode (2) and providing a solid dielectric (4) to the lower electrode (3). In the cas of

Fig. 1, a film is formed even more eff ctively by rotating the upper lectrode (1).

Usually, glow discharge is not produced easily under atmospheric pressur ; howev r, highly stable glow discharge and plasma formation are possible by using a inert gas, an el ctrode consisting of several fine wir s and a solid dielectric. For the substrate (5) it is possible to use, for example, suitable material of ceramics, glass, plastics or the like.

Furthermore, this invention also offers a method and apparatus which can produce a stable glow discharge plasma reaction at atmospheric pressure, without producing arc discharge, even through a conductive material such as a metal or alloy is used as a substrate.

This invention further offers an atmospheric pressure plasma reaction method characterised by treating the surface of the substrate by plasma produced at atmospheric pressure from a monomer gas introduced into a reaction vessel having a single dielectric-covered electrode, the surface of the upper electrode being covered with a solid dielectric, or a pair of dielectric-covered electrodes, the surface of each of upper and lower electrodes being covered with a solid dielectric respectively.

As a further preferred embodiment, a perforated pipe is provided in the vicinity of the substrate so that reaction gas diffuses uniformly. This apparatus is shown in Fig. 2.

Fig. 2 shows an example of the reaction apparatus of this invention in which a solid dielectric is provided on each of the upper and lower electrodes. This example has an upper electrode (12) an a lower electrode (13) to which high voltage is applied in the reaction vessel consisting of a bell jar (11) made from Pyrex glass.

Heat resistant solid dielectrics (14a) and 14b) made of glass, ceramics, plastics or mica are provided on the surface of the upper electrode (12) and lower electrode (13). A substrate (15) such as a plate is placed on solid dielectric (14b) provided on the upper surface of lower electrode (13).

The reaction gas consisting of a mixture of a rare gas such as He, Ne, Ar, etc., and reagent gas is introduced into a perforated pipe (18) having many openings (17) through a reaction gas inlet (16) so that the reaction gas diffuses from openings (17) uniformly onto the substrate (15). Unreacted gas, rare gas, etc. are discharged from exit (19) of the reaction vessel.

A temperature sensor (20) and a heater (21) are provided in the lower electrode (13). Installation of a cooling device is possible.

In this example, the reaction zone in the bell jar (11) is maintained at atmospheric pressure.

In general glow discharge is not produced easily at atmospheric pressure and when the substrate (15) is metal or alloy, arc discharge tends to occur when applying high voltage, thus making surface treatment of the substrate (15) difficult. In this embodiment, however, stable glow discharge at atmospheric pressure is facilitated even though the substrate (15) is metal, alloy or a conductive material such as silicon by providing the solid dielectrics (14a) and (14b) on the surface of the upper electrode (12) and lower electrode (13) respectively as shown in Fig. 2. Of course, if the substrate (15) is ceramics, glass, plastics, or the like, highly stable glow discharge can more readily be achieved.

For reagent gas, it is possible to use an arbitrary material from among saturated or unsaturated hydrocarbons such as methane, ethane, ethylene, propylene, etc., or hydrocarbons having substituents, e.g. halogenated hydrocarbon such as CF_4, C_2F_6, CHF_3 or SF_6, or other functional substituents, or gaseous compounds of semimetals such as Si and Ga, or gaseous metal compounds. Furthermore, oxygen, halogen, hydrogen, nitrogen or ammonia may be added.

The ratio of rare gas to reagent gas is not particularly critical. However, the preferred rare gas concentration is greater than 65%, more preferably higher than 90%. Several kinds of gases may be used as the reaction gas to be introduced.

Depending on types and reaction conditions of the reagent gas to be used, plasma polymer films, plasma reformed surface films and plasma etched films can be obtained.

As shown in Fig. 2, it is effective to form several grooves (22) on the lower surface of upper electrode (12). These grooves (22) are effective in diffusing the glow discharge (which is liable to concentrate at the edge and in the vicinity of the upper electrode (12)), and cause the discharge to diffuse uniformly over all the surface of the upper electrode (12). By these grooves (22), localized concentration of the glow discharge is prevented. Thus, a uniform film thickness is formed or uniform surface treatment is achieved on the surface of the substrate (15). The depth of these grooves (22) may be 1 to 2 mm. Furthermore, it is possible to decide the shape of these grooves (22) depending on the shape and properties of the substrate (15). For example, the grooves (22) may comprise several holes (23) as shown in Fig. 3 or several concentric circular grooves (24) as shown in Fig. 4.

The shape of an upper electrode (12) may be changed as shown in fig. 5. By this change, it is possible to increase the uniformity of the surface treatment.

Production of glow discharge has been difficult at atmospheric pressure. However, highly stable glow

discharg and formation of plasma become possible by using rare gas, providing solid dielectric on each of the lectrodes and forming several grooves on th lower surfac of the upper electrode. A suitable material of metal, alloy, ceramics, glass, plastics, or th like can be used as the substrate (15) shown in Fig. 2.

Fig. 7 shows an example of the reaction apparatus having a different structure from Fig. 2. The upp r electrode (12) rotates and reagent gas is introduced into the reaction zone through gas nozzle (25).

Fig. 10 shows an exampl in which the solid dielectric is provided only on the upper electrode. In other words, a heat resistant solid dielectric such as glass, ceramics, plastics or mica is provided on the surface of the upper electrode (12). The substrate (15) such as plate body is placed onto the upper surface of the lower electrode (13).

To obtain more stable plasma under the atmospheric pressure, it is effective to form several grooves (22) on the lower surface of the upper electrode (12) as shown in Fig. 11.

The grooves (22) are for uniformly diffusing the glow discharge which is liable to concentrate at the edge and in the vicinity of the upper electrode (12), in Fig. 2, and cause glow discharge to diffuse over all parts of the surface of the upper electrode (12). By these grooves (22), it is possible to prevent localized concentration of glow discharge, and to produce uniformly diffused stable glow discharges thus forming a uniform film thickness over the substrate (15) or to achieve uniform surface treatment.

The present invention is described further in detail by means of the following examples which are given by way of illustration only:-

EXAMPLE 1

With the use of the apparatus shown in Fig. 1 (electrode diameter: 30 mm, distance between electrodes: 10 mm), a polyethylene film was formed from ethylene monomer under the following conditions:

(a) Gas mixture:
He : : 4,500 SCCM
Ethylene : 3.6 SCCM
(b) Glow discharge:
Atmospheric pressure,
3,000 Hz, 1.05 kV, 3 mA,
(c) Substrate:
Cover glass

A polyethylene film was obtained on the substrate surface at a film forming rate of 12,500 A/2 hr. The film was transparent, with satisfactory adhesion.

EXAMPLE 2

A polyethylene film was formed in the same manner as in Example 1 under the following conditions:

(a) Gas mixture:
He : : 4,500 SCCM
Ethylene : 6.0 SCCM
(b) Glow discharge:
Atmospheric pressure,
3,000 Hz, 1.25 kV, 6 mA,
(c) Substrate:
Cover glass

A polyethylene film was obtained at a film forming rate of 2,100 A/2 hr. The film was transparent, with satisfactory adhesion.

EXAMPLE 3

A polyethylene film was formed in the same manner as in Example 1 under the following conditions:

(a) Gas mixture:
He : : 4,500 SCCM
Ethylene : 2.5 SCCM
(b) Glow discharge:
Atmospheric pressure,
3,000 Hz, 1.01 kV, 2.2 mA,
(c) Substrate:
Cover glass

A polyethylene film was obtained at a film forming rate of 16,800 A/5.5 hr. The film was transparent, with a satisfactory adhesion.

EXAMPLE 4

A polyethylene film was formed in the same manner as in Example 1 under the following conditions:
(a) Gas mixture:
He : : 4,500 SCCM
Ethylene : 3.6 SCCM
(b) Glow discharge:
Atmospheric pressure,
3,000 Hz, 1.1 kV, 3 mA,
(c) Substrate:
0.2 mm-thick quartz glass

A polyethylene film was obtained at a film forming rate of 9,000 A/2 hr. The film was transparent, with a satisfactory adhesion.

EXAMPLE 5

In the apparatus as shown in Fig. 2 using heat-resistant captone-covered electrodes having a diameter of 30 mm and a distance between electrodes of 10 mm (with no grooves (22)), a polyethylene film was formed from ethylene monomer under the following conditions:
(a) Reaction gas concentration (%):
Ethylene/He = 95/5
(b) Discharge:
Atmospheric pressure,
3,000 Hz, 1.05 kV, 3 mA,
(c) Substrate:
Aluminum substrate

A polyethylene film was thus formed on the surface of the aluminum substrate at a film forming rate of 11,417 A/2. The film was transparent, with excellent adhesion and a uniform film thickness.
In this Example, highly stable glow discharge took place without the occurrence of arc discharge, thus making available high-activity and high-stability plasma.

EXAMPLE 6

In the same manner as in Example 5, a polyethylene terephthalate film was treated under the following conditions, to make the surface thereof hydrophobic. Formation of a carbonfluorine reformed film was confirmed.
(a) Reaction gas concentration (%):

CF_4/He	=	91.6/8.4,
CF_4	:	10 ml/min,
He	:	216.7 ml/min,

(b) Discharge:
Atmospheric pressure,
3,000 Hz, 3.46 to 3.75 k.V, 8 mA,

The relationship between the treatment time and the contact angle is shown in Table 1. For comparison purposes, the contact angle for an untreated case is also shown in Table 1.

The surface having become hydrophobic was thus confirmed, with a uniform degree of treatment.

Table 1

Treating time	30 sec	1 min	5 min	Untreated
Contact angle	95.5°	96.0°	98.0°	64°

EXAMPLE 7 and 8

The same treatment as in Example 6 was applied to a conductive graphite (already wrapped) as the substrate, under the conditions as shown in Table 2.

The measurement of the contact angle in these Examples permitted confirmation of a high degree of hydrophobicity. The result is shown in Table 2.

In an apparatus comprising electrodes not using solid dielectric, production of arc discharge made it impossible to carry out the plasma treatment.

Table 2

Item	Example	Example 7	Example 8	Case for Comparison
Reaction gas flow rate				
CF_4		93.6 ml/min	93.6 ml/min	-
He		216.7 ml/min	216.7 ml/min	-
Discharge (atmospheric pressure)				
Current		10 mA	3 mA	-
Voltage		3.99 kV	2.74 kV	-
Treating		5 min	20 min	-
Contact angle		128°	137°	68°

EXAMPLE 9 and 10

With the use of the reaction apparatus shown in Fig. 2, with grooves (22) in one case and without grooves (22) in another case, a plasma-polymerized polyethylene film was formed on a silicon substrate.

(a) Reaction gas (%):

C_2H_4	:	3.6 ml/min,
He	:	4,495 ml/min,

(b) Discharge:
3,000 Hz, 1.5 hr,
Atmospheric pressure, room temperature.

The relationship between the transverse distance of the silicon substrate and the thickness of the plasma-polymerized polyethylene film is shown in Fig. 6.

As is clear from Fig. 6, comparing the case (a) using the reaction apparatus without grooves (22), with the case (b) using an upper electrode with concentric circular grooves (24) (as shown in Fig. 4) shows that the latter permit more uniform film thickness distribution, suggesting that plasma is stabilized over the entire surface of the substrate.

EXAMPLE 11

A SiN_x film was formed with the use of the apparatus shown in Fig. 7 under the following reaction conditions:

He	:	5,000 ml/min,
H_2	:	20 ml/min,
N_2	:	20 ml/min,
$SiCl_4$	:	4.5 mg/min,
Pressure	:	Atmospheric pressure,
RF	:	13.56 MHz, 220 W,
Temperature	:	440 °C
Substrate	:	Si Wafer.

Fig. 8 illustrates the difference in IR of the SiN_x film thus obtained from the silicon substrate.

As Si-N expansion-concentration movement is observed at about 850 cm^{-1}, and an Si-O expansion-contraction movement, at 1020-1090 cm_{-1}.

Fig. 9 shows the result of XPS analysis in the depth direction of the SiN_x film, which permits confirmation that nitrogen is contained in a large quantity. The film has the composition SiN_xO_y, and the content of oxygen thereof is controllable.

EXAMPLE 12

With the use of the apparatus shown in Fig. 10 using heat-resistant captone-covered electrodes having a diameter of 30 mm and a distance between electrodes of 10 mm, a polyethylene film was formed from ethylene monomer under the following conditions:

(a) Reaction gas flow rate:

C_2H_4	:	3.0 SCCM,
He	:	4,500 SCCM,

(b) Discharge:
Atmospheric pressure, room temperature,
3,000 Hz, 1.0 kV,
1 to 5 mA (gradually increased),

(c) Substrate:
Silicon substrate

A polyethylene film was formed on the silicon substrate at a film forming rate of 10,000 to 20,000 A/hr.

The film was transparent, with satisfactory adhesion and a uniform film thickness.

In this example, highly stable and uniformly dispersed glow discharge took place without the occurrence of arc discharge, thus making available high-activity and high-stability plasma.

EXAMPLE 13

In the same manner as in Example 12, a polyethylene terephthalate film was formed under the following conditions to make the surface thereof hydrophobic:

(a) Reaction gas flow rate:

CF_4	:	25 SCCM,
He	:	210 SCCM,

(b) Discharge:
Atmospheric pressure,
3,000 Hz, 3.5 kV,
2 to 8 mA (gradually increased).

The contact angle was measured five minutes after the start of treatment. The result showed a contact angle of 98° C. A non-treated film had a contact angle of 64°. The surface having become hydrophobic was thus confirmed. Treatment was uniform.

EXAMPLE 14

The same manner as in Example 13 was applied to a conductive graphite (already wrapped) as the substrate.

(a) Reaction gas flow rate:

CF_4 : 96 SCCM,
He : 220 SCCM,

(b) Discharge:
Atmospheric pressure,
3,000 Hz, 2.8 kV,
3 to 5 mA (gradually increased).

The contact angle was measured 15 minutes after the start of treatment. The result showed a contact angle of 131° C. A non-treated film had a contact angle of 68°. The surface having become hydrophobic was confirmed. Treatment was uniform. In this Example, highly stable and uniformly dispersed glow discharge took place without the occurrence of arc discharge as in the Example 12, thus making available high-activity and high-stability plasma.

The present invention is not limited to the above-mentioned examples. Variations are possible within the framework of the present invention in such details as the size and shape of the reaction vessel, the structure, configuration and shape of the electrodes, the shape and number of grooves on the lower surface of the upper electrode, and the structure and configuration of the reaction gas supply.

According to the present invention, as described above in detail, it is possible, as compared with the conventional low-pressure glow discharge plasma reaction, to eliminate the necessity of an apparatus and facilities for forming a vacuum system, reduce the cost, and carry out film formation and/or surface treatment under the atmospheric pressures, requiring only a relatively simple structure and configuration of the apparatus and facilitating treatment of a large-area substrate because the substrate can be set directly on the upper surface of the lower electrode.

Furthermore, the present invention allows film formation and/or surface treatment without limiting the material, shape and prop rties of the substrate and makes available uniform film thickness and surface condition in a thin film so obtained.

Claims

1. A method of treating the surface of a substrate with reactive plasma which comprises exciting a reagent gas in a reaction vessel having a pair of opposing lectrodes to produce glow discharge plasma at atmospheric pressure and causing or permitting the plasma to contact the surface of said substrate.

2. A method as claimed in claim (1), wherein: a thin film is formed on the surface of said substrate.

3. A method as claimed in claim (1), wherein: the surface of said substrate is chemically changed.

4. A method as claimed in claim (1), for forming a thin film on a substrate which comprises introducing a monomer gas in admixture with an inert gas into a reaction vessel having an upper electrode comprising a plurality of vertical fine wires to convert the gas into plasma at atmospheric pressure, thereby forming a thin film on the surface of the substrate.

5. A method as claimed in claim (4), wherein a solid dielectric is provided on the upper surface of a lower electrode on which said substrate is to be set.

6. A method as claimed in claim (1), which comprises introducing a mixture of a rare gas and a reagent gas into a reaction vessel having a pair of dielectric-covered electrodes formed by providing a solid dielectric on the surface of each of an upper electrode and a lower electrode, and exciting the gas to form plasma at atmospheric pressure, thereby treating the surface of a substrate on said vessel.

7. A method as claimed in claim (1), which comprises introducing a reagent gas into a reaction vessel having a single dielectric-covered electrode comprising an upper electrode, the surface of which is covered with a solid dielectric, and plasma-exciting said reagent gas at atmospheric pressure, thereby treating the surface of a substrate in said vessel.

8. A polyalkylene or polyfluoroalkylene polymerized film formed through glow discharge plasma reaction at atmospheric pressure.

9. A carbon-fluorine reformed film formed by surface reforming by a glow discharge plasma reaction at atmospheric pressure.

10. A SiN_x film formed by a glow discharge plasma reaction at atmospheric pressure.

11. An amorphous carbon film formed by a glow discharge plasma reaction at atmospheric pressure.

12. An amorphous silicon film formed by a glow discharge plasma reaction at atmospheric pressure.

13. An apparatus for treating the surface of a substrate with a reactive plasma at atmospheric pressure which comprises a reaction vessel provided with an upper and a lower electrode, the upper electrode being formed from fine vertical wires.

14. An apparatus for treating the surface of a substrate with a reactive plasma at atmospheric pressure which comprises a reaction vessel provided with an upper and a lower electrode and a perforated pipe for uniformly dispersing a gas near the surface of a substrate placed in the reaction vessel.

15. An apparatus as claimed in claim 13 or claim 14, wherein a solid dielectric is arranged on the upper surface of the lower electrode.

16. An apparatus as claimed in claim 13 or claim 14, wherein the upper and lower electrodes are covered with dielectric.

FIG. 1

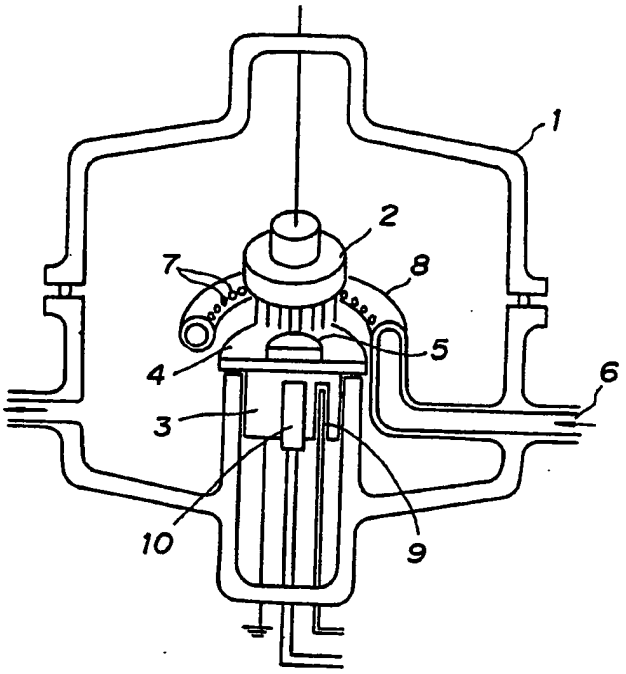


FIG. 2

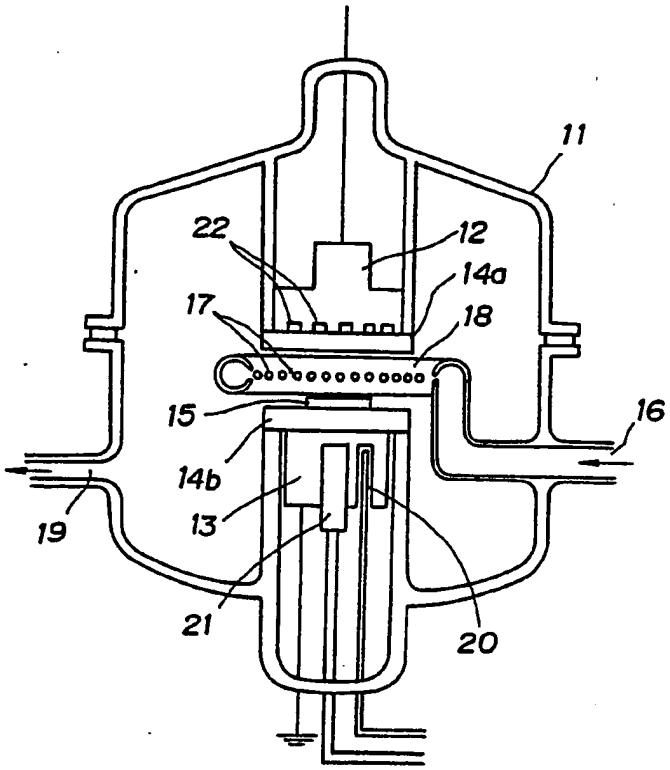


FIG. 3

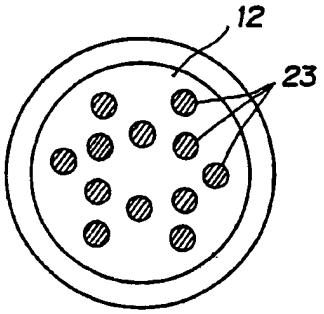


FIG. 4

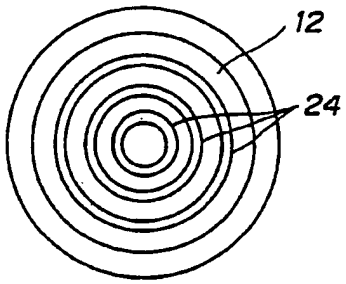


FIG. 5

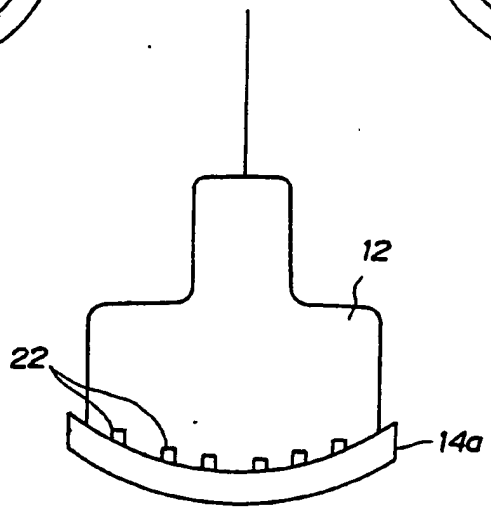


FIG. 6

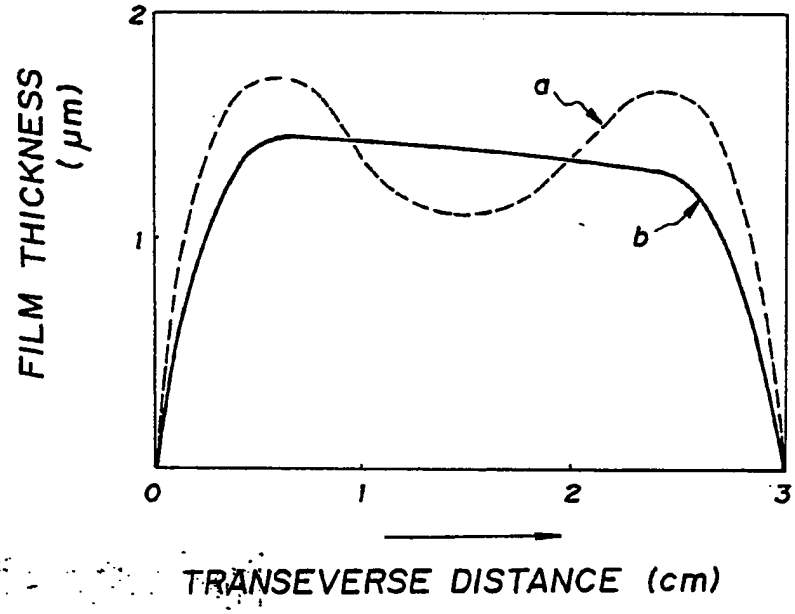


FIG. 7

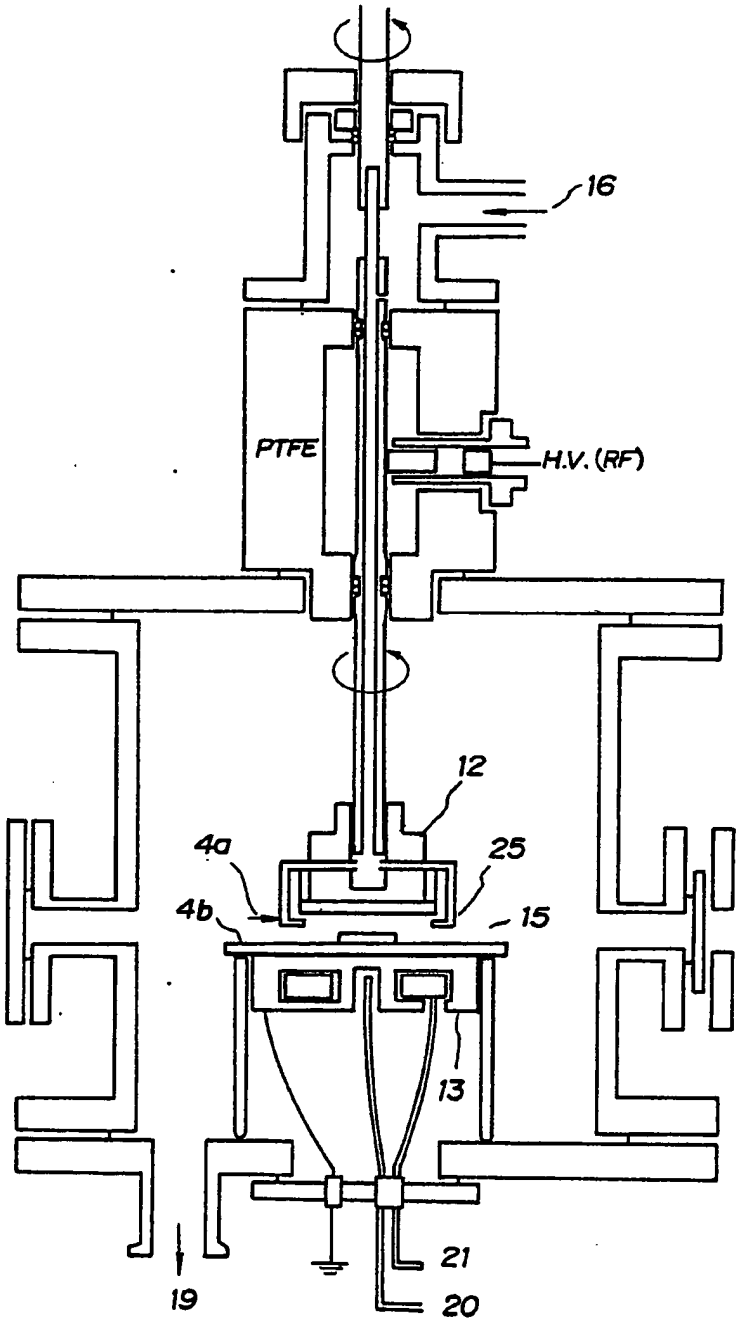


FIG. 8

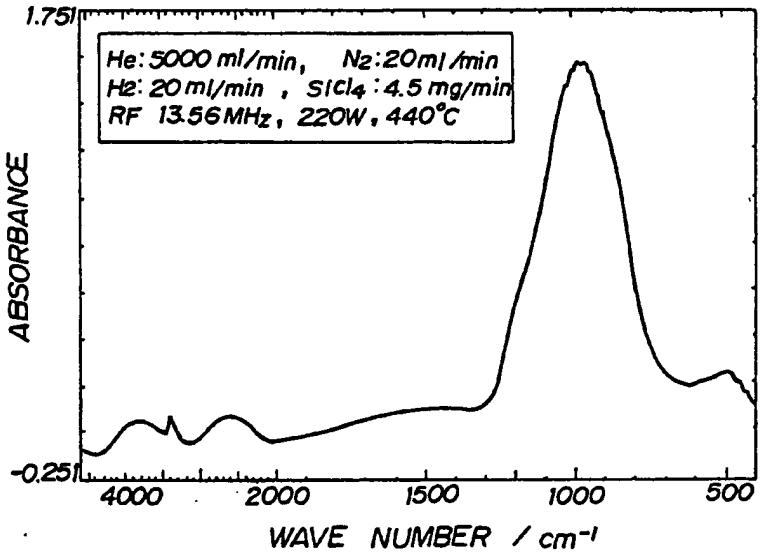

1.75
-0.25
ABSORBANCE
He: 5000 ml/min, N2: 20ml/min
H2: 20 ml/min , SiCl4 : 4.5 mg/min
RF 13.56MHz, 220W, 440°C
4000
2000
1500
1000
500
WAVE NUMBER / cm-1

FIG. 9

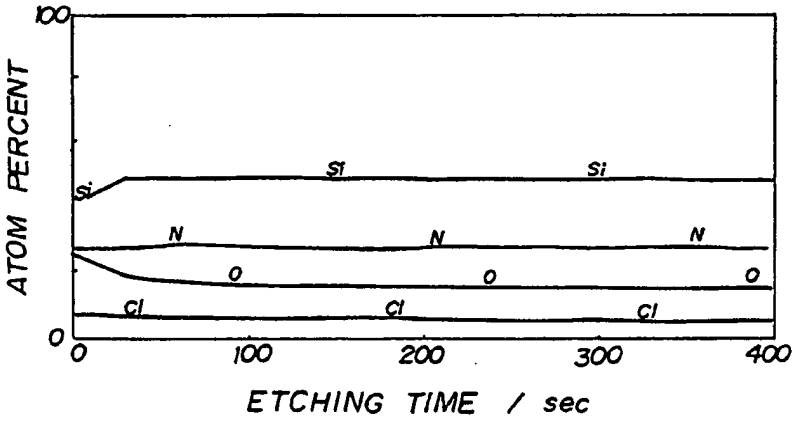

100
0
ATOM PERCENT
Si
Si
Si
N
N
N
O
O
O
Cl
Cl
Cl
0
100
200
300
400
ETCHING TIME / sec

FIG. 10

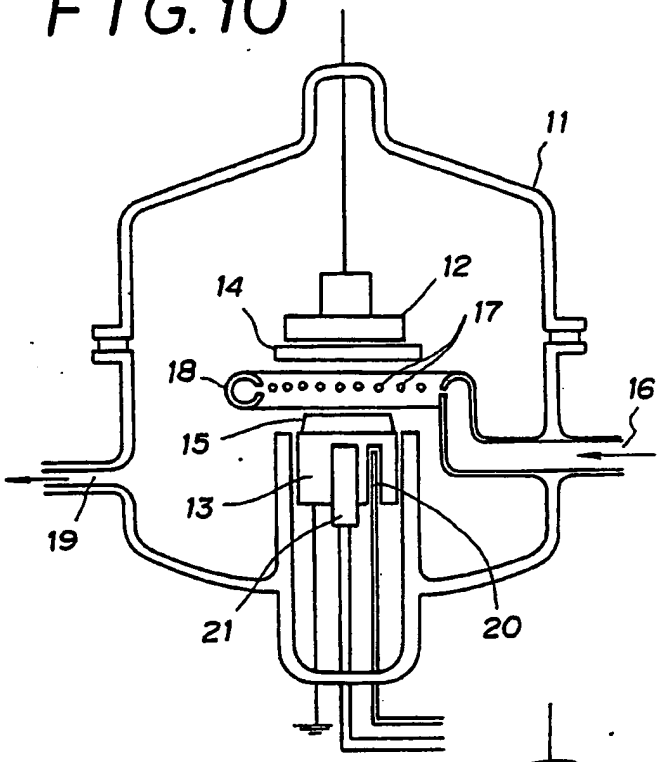


FIG. 11